

EFFECT OF ORGANOMETALLIC CATALYSTS ON COAL LIQUEFACTION AND PRODUCT DISTRIBUTION

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INTRODUCTION

Coal hydrogenation remains an attractive and potentially useful source of liquid fuels. There have been a number of studies on the comparative effectiveness of various catalysts and the results have been reviewed from time to time (1-5). A significant finding which has emerged from such studies is the importance of catalyst distribution. For example, in the hydrogenation of Rock Springs coal, nickelous chloride was found to be an ineffective catalyst when added as a powder, however, it was quite effective when it was impregnated on coal (6).

Because of their compatibility with the pasting oil which is used to slurry coal in hydrogenation studies, organometallic compounds would seem to be able to disperse better and therefore might be expected to be more effective catalysts.

Coal can be regarded as a highly cross linked "polymer" in which condensed aromatic rings are linked to one another through hydroaromatic or heteroatom linkages (7,8). On heating, weak bonds break leading to free radicals which can be stabilized by transfer of hydrogen to give soluble products or they may recombine to form insoluble chars (9). The hydrogen which is transferred to the radical could come from coal itself, donor solvent or molecular hydrogen. It is possible that some organometallics might be able to generate an intermediate under liquefaction conditions which might be an effective hydrogen transfer agent (10).

A few reports on the use of organometallics in coal liquefaction have been published. It appears that at temperatures less than 350°C such catalysts are ineffective (11). However, at higher temperatures some organometallics were found to aid coal liquefaction (12). Metal naphthenates of molybdenum, nickel, tin, iron and cobalt produced conversions exceeding 80 percent at 500°C, zero time at temperature (4).

In the present study we have assayed the catalytic activity of a variety of organometallic compounds in the liquefaction of two New Mexico coals. We have also examined their effect on the proportion of asphaltene and oil produced.

EXPERIMENTAL

Parr 4022 pressure reactor with 1 liter T316 stainless steel bomb, 2250 watt heater and 0-600°C automatic temperature controller was used in all hydrogenation experiments. In order to avoid catalyst memory effects, the reactants were placed in a glass vessel (liner) which fitted snugly inside the bomb.

A sub-bituminous coal from Navajo Mine (South Barber Seam 8) and a bituminous high volatile coal from York Canyon seam in Raton Formation were used in our studies. Ultimate analysis of the coals is given in Table 1.

Into the glass container 15g of -60 mesh coal, catalyst (1% of maf coal) and 45g tetrahydronaphthalene (THN) were placed. The container was put in the steel bomb and the bomb was pressurized with hydrogen to 1500 psi after flushing to remove air. It was then heated to the designated temperature and kept at that temperature for the selected reaction time. The reactants were kept mixed by the rocking motion of the pressure reactor. After the reaction, the bomb was cooled to room temperature and contents flushed with benzene and filtered. The filter-cake was extracted in a soxhlet extractor for 24 hours, dried and weighed to obtain the weight of unreacted coal and ash. After distilling off benzene from the filtrate and the soxhlet extract, pentane was added to precipitate asphaltene which was filtered and dried to a constant weight at 50°C at 3mm in a vacuum oven.

After distilling pentane from the filtrate through a vigreux column, as much of THN as possible was removed by distillation under vacuum (16mm) and an oil bath temperature of 120°C. A weighed amount of methyl-naphthalene (MN) was added to the residue which was thinned with chloroform and analyzed by gas liquid chromatography.

From the areas of the peaks of THN and MN the amount of THN present was calculated using a correction factor determined previously from a mixture of known amounts of THN and MN. Difference in the weight of the vacuum distillation residue and the amount of THN gave the amount of oil present.

The results were calculated as follows:

Percent Conversion = $(\text{maf coal} - \text{unreacted coal}) \times 100 / \text{maf coal}$

Percent yield asphaltene = $\text{wt. of asphaltene} \times 100 / \text{coal converted}$

Percent yield oil = $\text{wt. of oil} \times 100 / \text{coal converted}$

Percent conversion asphaltene = $\text{wt. of asphaltene} \times 100 / \text{maf coal originally present}$

Percent conversion oil = $\text{wt. of oil} \times 100 / \text{maf coal originally present}$

RESULTS AND DISCUSSION

Effect of Catalysts on Coal Conversion: For the Navajo Mine coal (Table 2) organometallic compounds of palladium, rhenium, iridium, molybdenum, rhodium, iron, cobalt, tin and nickel were found to be effective catalysts. Organometallic compounds of germanium, tungsten, gallium, arsenic had moderate catalytic activity whereas the organometallic compounds of copper, lead, zinc and manganese had marginal or no catalytic activity.

For the York Canyon Mine coal (Table 3) organometallic compounds of iridium, rhodium, molybdenum and nickel showed good catalytic activity. Organometallic compounds of germanium, nickel, gallium and antimony were found to be moderately active whereas compounds of arsenic, copper, lead, manganese, chromium and zinc had no or marginal catalytic activity.

Of the other catalysts tested, stannous chloride was found to be an excellent catalyst in agreement with other reports in literature and was used as a standard of comparison. Ammonium molybdate on the other hand was found to have marginal catalytic activity.

Effect of Catalysts on Product Distribution: Hydroliquefaction of coal is the net result of a complex series of parallel or sequential reactions including hydrogenation, thermal fragmentation, disproportionation and stabilization of free radicals etc. It was thought that different catalysts would affect many of the above reactions to varying degrees and thus change the proportion of asphaltene, oil and gas produced.

In our experiments the product of liquefaction was partitioned into asphaltene and oil and the amount of each was determined by the procedures described in the experimental section. Percent of the product found as asphaltene and oil are shown in Table 4.

In uncatalyzed hydrogenation of York Canyon Mine coal the ratio of asphaltene to oil produced is 1.7 whereas for most of the active catalysts the ratio is 1.8-2.5. Thus many of the catalysts produce slightly more asphaltene than the uncatalyzed hydrogenation. Also the sum of asphaltene and oil yield is nearly 100 percent. This indicates that very little gaseous products are formed in hydrogenations at 380°C for 6 hours.

These results can be accommodated in the free radical mechanism of coal liquefaction. At high temperature coal substance fragments into free radicals which are stabilized by transfer of hydrogen to yield asphaltene, oil and gaseous products. In the absence of a catalyst some of these radicals may combine to produce insoluble char. In the presence of a catalyst, more of these radicals are stabilized by hydrogen transfer to produce soluble products.

Effect of Reaction Time and Temperature: York Canyon Mine coal was hydrogenated for various lengths of time in the absence and also in the presence of molybdenum hexacarbonyl as a catalyst. The results show (Fig. 1) that the amount of asphaltene increases, reaches a maximum and then decreases with time. The increase in asphaltene in the initial stages of the reaction and its decrease in the later stages is faster in the catalyzed than in the uncatalyzed hydrogenation. Thus a catalyst not only helps to liquefy coal, it also helps to convert asphaltene into oil.

Paralleling above results, the amount of oil produced (Fig. 1) also increases with time and the increase is faster in the presence of a catalyst than in its absence.

The effect of temperature on the product distribution in some catalyzed and

uncatalyzed hydrogenations is shown in Fig. 2. As noted before, more asphaltene is produced in the early stages of the reaction in the catalyzed than in the uncatalyzed process. In the later stages of the reaction asphaltene is converted faster into oil and gaseous products in the catalyzed than in the uncatalyzed reactions. Molybdenum hexacarbonyl appears to be a better catalyst in this respect than stannous chloride.

The sum of the percent of product found to be asphaltene and oil (Table 5) decreases with time and with increase in temperature. This indicates that asphaltene and oil are being converted into gaseous products at higher temperatures and longer reaction times. Comparison of the catalyzed with the uncatalyzed hydrogenations shows that more gaseous products are formed in the former than in the latter case, and again molybdenum hexacarbonyl is more effective in this respect than stannous chloride.

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TABLE 1 Ultimate Analysis of Coals

Navajo Mine (South Barber Seam S)	Coal
	wt %
Moisture	8.62
Carbon	57.00
Hydrogen	3.07
Nitrogen	1.17
Sulfur	0.74
Ash	15.77
Oxygen (diff.)	<u>13.63</u>
	100.00

York Canyon Mine Coal	wt %
Moisture	1.57
Carbon	63.89
Hydrogen	4.42
Nitrogen	1.35
Sulfur	0.44
Ash	22.30
Oxygen (diff.)	<u>6.05</u>
	100.00

TABLE 2 Effectiveness of Catalysts in the Hydrogenation of Navajo Mine Coal
Hydrogen pressure initial (cold): 1500 psi; Catalyst: 1% naf coal;
Time: 6 hours; Solvent: Tetrahydronaphthalene; Temperature: 350°C.

No.	Catalyst	Percent Conversion
1.	None	61
2.	$(C_6H_5)_3As$	68
3.	$Co(C_5H_9O)_3$	74
4.	$CoCl_2 \cdot 6H_2O$	73
5.	$Cu(C_6H_5O)_2$	67
6.	$Fe(C_6H_5O)_3$	75
7.	$FeCl_3 \cdot 6H_2O$	67
8.	$Ga(C_6H_5O)_3$	69
9.	$(C_6H_5)_4Fe$	69
10.	$[Ir(CO)_2Cl]_x$	83
11.	$Mn(C_6H_5O)_2$	63
12.	$Mo(CO)_6$	79
13.	$(NH_4)_6Mo_7O_{24} \cdot 11H_2O$	66
14.	$Ni(C_6H_5O)_2$	73
15.	$NiCl_2 \cdot 6H_2O$	67
16.	$Pb(C_6H_5O)_2$	66
17.	$(C_6H_5)_4Pb$	63
18.	$Pd(C_6H_5O)_2$	84
19.	$Re_2(CO)_{10}$	84
20.	$Rh(C_6H_5O)_3$	82
21.	$SnCl_2 \cdot 2H_2O$	75
22.	$(C_6H_5)_3Sn$	73
23.	$(C_6H_5)_3SnH$	67
24.	$W(CO)_6$	68
25.	$Zn(C_6H_5O)_2$	64
26.	$ZnCl_2$	65

TABLE 3 Effectiveness of Catalysts in the Hydrogenation of York Canyon Nine Coal

Hydrogen pressure initial: 1500 psi; Catalyst: 1% maf coal; Solvent: Tetrahydronaphthalene; Temperature: 380°C; Time: 6 hours

No. Catalyst	Percent Conversion
1. None	44
2. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	72
3. $(\text{C}_6\text{H}_5)_3\text{As}$	53
4. $\text{Co}(\text{C}_5\text{H}_5\text{O}_2)_3$	63
5. $\text{Co}_2(\text{CO})_8$	74
6. $\text{Cu}(\text{C}_6\text{H}_5\text{O}_2)_2$	53
7. $\text{Cr}(\text{C}_8\text{H}_{15}\text{O}_2)_3$	47
8. $\text{Cr}(\text{CO})_6$	48
9. $\text{Fe}(\text{C}_5\text{H}_5\text{O}_2)_3$	51
10. $\text{Fe}(\text{C}_8\text{H}_{15}\text{O}_2)_3(1\frac{1}{2}) + \text{I}_2(0.55)$	76
11. $\text{Fe}(\text{CO})_5$	58
12. $\text{Ga}(\text{C}_5\text{H}_5\text{O}_2)_3$	61
13. $\text{Ge}(\text{C}_6\text{H}_5)_4$	64
14. $\text{I}_2(0.55)$	72
15. $\text{In}(\text{C}_5\text{H}_5\text{O}_2)_3$	59
16. $\text{Ir}(\text{CO})_3\text{Cl}$	77
17. $\text{Mn}(\text{C}_6\text{H}_{11}(\text{CH}_2)_3\text{COO})_2$	47
18. $\text{Ni}_4\text{Mo}_2\text{O}_{24} \cdot 2\text{H}_2\text{O}$	46
19. $\text{Mo}(\text{CO})_6$	73
20. $\text{Mo}(\text{CO})_6(1\frac{1}{2}) + \text{I}_2(0.55)$	80
21. $\text{Ni}(\text{C}_8\text{H}_{15}\text{O}_2)_2$	67
22. $\text{Pd}(\text{C}_6\text{H}_{11}(\text{CH}_2)_3\text{COO})_2$	49
23. $\text{Pd}(\text{C}_5\text{H}_5\text{O}_2)_2$	72
24. $\text{Re}_2(\text{CO})_{10}$	74
25. $\text{Rh}(\text{C}_5\text{H}_5\text{O})_3$	75
26. $\text{Ru}_3(\text{CO})_{12}$	75
27. $\text{Sn}(\text{C}_6\text{H}_5)_4$	46
28. $\text{Sn}(\text{C}_6\text{H}_5)_4$	58
29. $\text{W}(\text{CO})_6$	74
30. $\text{Zn}(\text{C}_{10}\text{H}_{15}\text{O}_2)_2$	43

TABLE 4 Effect of Catalysts on the Percent Yield of Asphaltene and Oil from York Canyon Nine Coal.

No. Catalyst	%Conversion	%Yield Asph.	%Yield Oil	%Yield Asph-Oil	%Asph-Oil
1. None	48	64	38	102	1.7
2. $\text{Co}_2(\text{CO})_8$	74	69	29	98	2.4
3. $\text{Cr}(\text{C}_8\text{H}_{15}\text{O}_2)_3$	50	41	59*	---	0.7
4. $\text{Fe}(\text{C}_5\text{H}_5\text{O}_2)_3$	48	60	33	99	2.0
5. $\text{Fe}(\text{C}_8\text{H}_{15}\text{O}_2)_3(1\frac{1}{2}) + \text{I}_2(0.55)$	76	65	36	101	1.8
6. $\text{Ga}(\text{C}_5\text{H}_5\text{O}_2)_3$	61	70	36	106	1.9
7. I_2	72	61	41	102	1.5
8. $\text{In}(\text{C}_5\text{H}_5\text{O}_2)_3$	59	31	68*	---	0.4
9. $\text{Ir}(\text{CO})_3\text{Cl}$	77	65	34	99	1.9
10. $\text{Mo}(\text{CO})_6$	75	68	32*	---	2.1
11. $\text{Mo}(\text{CO})_6(1\frac{1}{2}) + \text{I}_2(0.55)$	80	71	32	103	2.2
12. $\text{Ni}(\text{C}_8\text{H}_{15}\text{O}_2)_2$	64	73	29	102	2.5
13. $\text{Pd}(\text{C}_5\text{H}_5\text{O}_2)_2$	73	61	36	97	1.7
14. $\text{Re}_2(\text{CO})_{10}$	73	64	36	100	1.8
15. $\text{Rh}(\text{C}_5\text{H}_5\text{O}_2)_3$	75	46	54*	---	0.9
16. $\text{Ru}_3(\text{CO})_{12}$	75	61	37	98	1.6
17. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	73	72	30	102	2.4

* values of Percent yield oil were obtained as follows:

$$100 - \% \text{ yield asphaltene} = \% \text{ yield oil}$$

TABLE 5 Effect of Time and Temperature on the Sum of the Percent Yield of Oil and Asphaltene in the Hydrogenation of York Canyon Nine Coal.

Catalyst	PERCENT YIELD (OIL + ASPHALTENE)			
	None	$\text{Mo}(\text{CO})_6$	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	
Temp., °C.	380 400 420	380 400 420	380 400 420	
Time hr				
1	- 100 110	- 95 97	- 98 99	
6	102 91 89	100 91 85	102 91 90	
24	92 86 78	90 78 59	- 79 90	

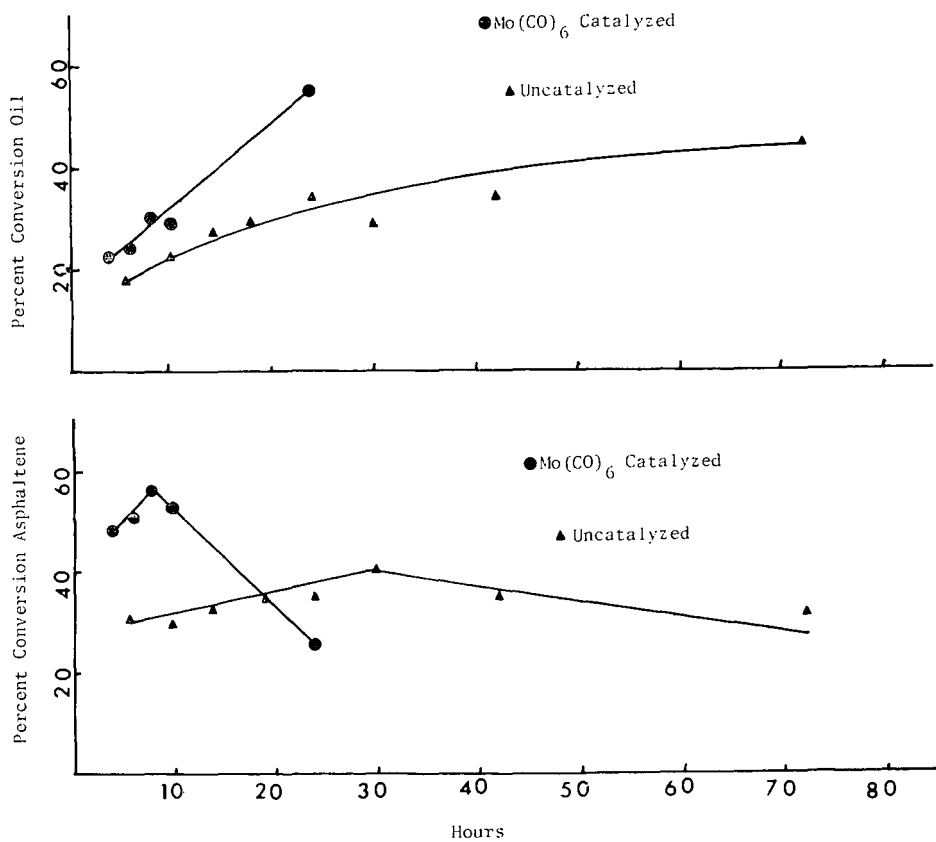


Fig. 1 Percent Conversion Asphaltene and Oil in the Hydrogenation of York Canyon Mine Coal.

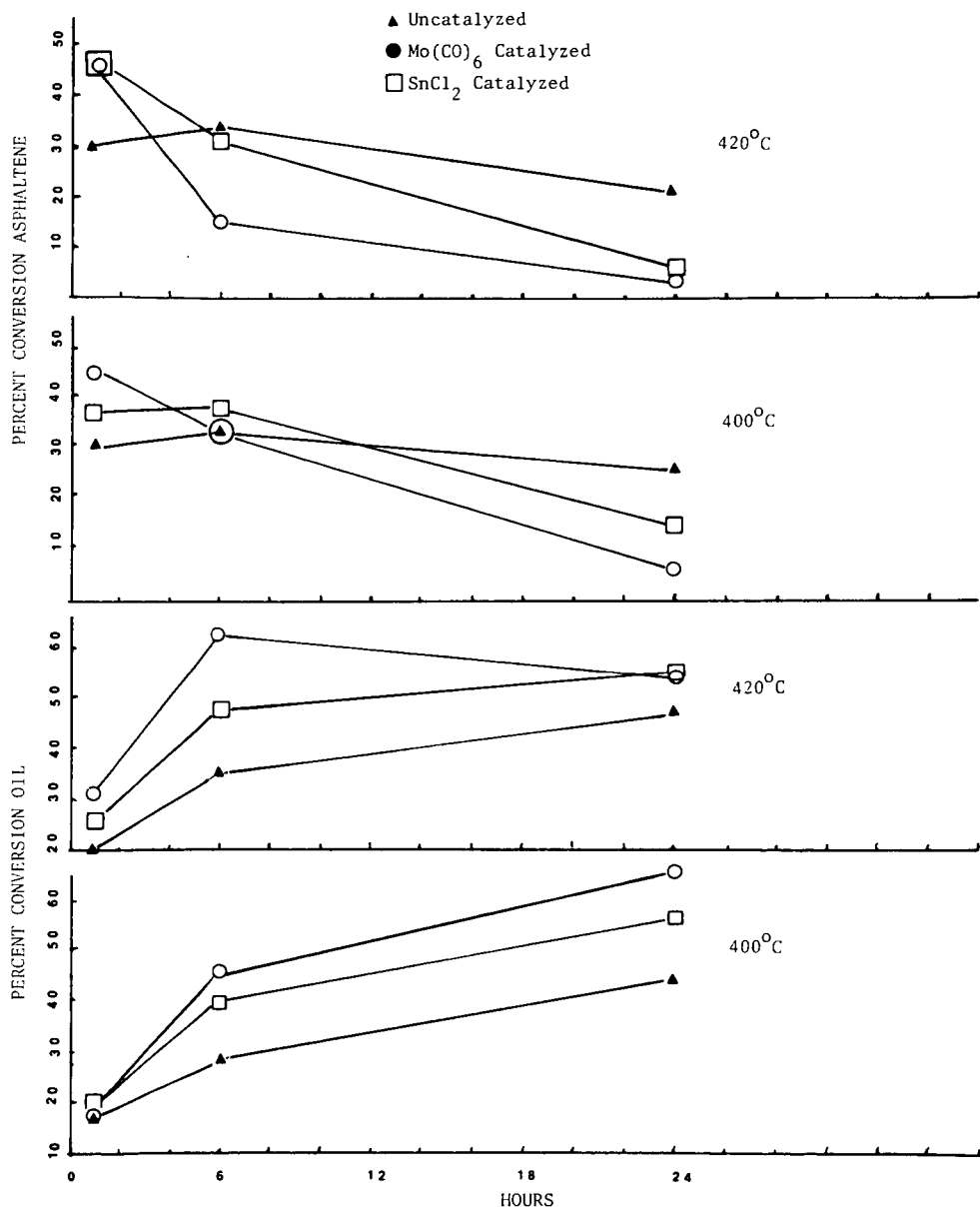


Fig. 2 Effect of Temperature and Reaction Time on the Percent Conversion Oil and Asphaltene.